

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Improvements in the Coating of Metals

We, THE PYRENE COMPANY LIMITED, a British Company of, Great West Road, Brentford, Middlesex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is well known to form protective coatings on metal surfaces by treating the surfaces with conversion coating solutions containing materials which will react with the metal of the metal surface to form an insoluble coating. Such coatings are very frequently formed on surfaces of metals such as zinc, iron and aluminium. However, it is not always easy readily to produce coatings having satisfactory properties. For instance, on zinc it is often difficult to produce a coating which is sufficiently heavy and uniform. Also, conversion coatings formed on metal surfaces often are not very adherent, so that they do not form a satisfactory base for paint or other organic finish. In general these difficulties have been particularly marked when the metal surface to be coated is in the form of a continuously moving strip or sheet. In such instances it is clearly necessary that the coating formation should be accomplished in the minimum time possible.

Individual conversion coating processes are generally applicable only to one particular metal, but it often happens that it would be convenient to have a process suitable for treating a number of different metals without modification. Thus, it often happens that in installations which treat predominantly zinc surfaces, such as those resulting from electroplating or hot dip galvanising of steel or other ferrous surface it is desirable to treat also surfaces which are predominantly of iron or aluminium.

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According to the present invention a process for forming a protective coating on a metal surface comprises preheating the metal and spraying onto it a conversion coating solution of which the principal coating-forming ingredient is a coating phosphate, a coating oxalate, a coating acetate or phosphoric acid with an auxiliary acid, the temperature of the metal and the quantity of the solution applied being such that there is substantially no run-off of solution and a dry conversion coating is formed part of which at least is soluble, and then, without any intermediate rinsing step, rendering the coating totally insoluble by applying to it an insolubilising solution which reacts with the soluble components of the conversion coating to form insoluble products.

The metal surface onto which the solution is applied is preferably preheated to a temperature of at least 175°F, usually to a temperature of between 200 or 600°F or, more preferably between 275 and 425°F. The quantity of solution sprayed and the temperature of the metal are arranged such that there is substantially no liquid run-off from the surface, and it is found that a dry, substantially uniform coating may be formed. The solution is preferably sprayed in such a way that it is, in effect, applied as a mist, for example by gas atomisation such that the droplets of the mist have a size between 15 and 350 microns. Such a process is described in Specification No. 863,098. The conditions of operation are arranged in such processes that the droplets of coating solution deposited on the metal surface dry on the surface substantially in the positions in which they initially strike the surface.

The spraying may be conducted in any suitable manner, but the particular mode of operation will usually depend on the type

of articles being treated. Thus, small articles may be sprayed by hand with one or more passes of the spray while articles in the form of strips or sheets may be passed continuously through one or more stationary spraying zones. When the metal surfaces to be sprayed are galvanised surfaces produced by hot galvanising it is particularly convenient to spray the surfaces while they are still hot from the galvanising.

The auxiliary acid included with phosphoric acid in the conversion coating solutions based on those two materials as the principal coating forming ingredients may be organic or inorganic. Examples of suitable acids are nitric acid, acrylic acid, methacrylic acid, polyacrylic acid, adipic acid, acetic acid, hydroxyacetic acid, gluconic acid, fumaric acid, maleic acid, malic acid, malonic acid, lactic acid, itaconic acid, tartaric acid, ethylene diamine tetraacetic acid, citric acid, hydroxymethyl phosphonic acid, oxalic acid, and chromic acid. Typically, these acids may be present in amounts to provide a ratio of  $\text{PO}_4$  ions to acid in the range of about 100:1 to about 2:1, with amounts sufficient to provide a ratio of from about 10:1 to about 4:1 being preferred.

Materials which can be used as coating phosphates, oxalates and acetates for forming conversion coatings on metals are well known and generally comprise the phosphate, oxalate or acetate of a metal in an aqueous acidic solution. For example the principle coating forming ingredient may be zinc phosphate, ferrous phosphate, ferric phosphate, nickel phosphate, manganese phosphate, calcium phosphate, chromium phosphate, cobalt phosphate, aluminium phosphate, cadmium phosphate, or ferric oxalate. Mixed metallic phosphates such as zinc phosphate, zinc iron phosphate, zinc calcium phosphate, iron manganese phosphate, may also be used.

It is sometimes desirable to include in the conversion coating solution based on a coating phosphate auxiliary acid such as is listed above in amounts such as those mentioned. This inclusion is particularly desired when the conversion coating solution contains iron.

The conversion coating solutions generally contain from 0.1 to 10.0%, preferably 0.3 to 6.0%, by weight phosphate or phosphoric acid (measured as  $\text{PO}_4$ ).

In addition to coating phosphates or phosphoric acid and auxiliary acid the conversion coating solutions may also contain various other materials, for example accelerators. Such materials which may be included include nitrates, nitrites, sulphites, halides and halates, e.g. bromides, chlorates, bromates, perchlorates, iodates and periodates, peroxides, permanganates, organic nitro compounds such as m-nitrobenzene sulphonate, nitro guanidine, nitro methane, nitro ethane, 1-nitro propane, nitrobenzene, o-nitro benzaldehyde, p-nitro-

phenol, p-nitro aniline, p-nitrochloro benzene, and picric acid. Other additives which may be used in the composition are those which increase the etching tendency of the solution, such as the so-called double fluorides, including fluosilicates, fluoborates, fluotitanates, fluostannates, fluozirconates, and fluovanadates.

These additional materials are most conveniently added to an acidic solution of the coating phosphate or phosphoric acid in a form which is readily dispersible in the acidic aqueous solution. Many water dispersible forms of these compounds may be used provided they have no adverse effect on the coating composition, the metal substrate, or the coatings subsequently produced or applied. Typically, such additives may be present in the conversion coating composition in amounts within the range of 0.01 to 6.0 percent by weight, and desirably in amounts within the range of 0.02 to 4.0 percent by weight.

Conversion coating compositions based on coating phosphates are preferably used at pH values from 0.7 to 3.5 while those based on phosphoric acid are preferably used at pH values of from 0.3 to 5.5 and the solutions are preferably applied in such a manner so as to obtain a coating weight of phosphate ions of from 10 to 250 milligrams per square foot of metal surface being treated. Desirably, the coatings obtained contain phosphate in the range of about 20 to 100 milligrams per square foot.

Part at least of the conversion coatings produced in the invention are water soluble and the coatings are rendered insoluble by application of an insolubilising solution. A wide range of methods of effecting the insolubilisation may be used, it merely being necessary that the result shall be that it shall not be possible to dissolve out part of the resulting coating. Thus this step of insolubilising the coating can be considered to be one of immobilising or fixing the coating on the metal surface. The effect of this step is to make the previously applied phosphate coating more adherent to a subsequently applied paint or similar protective coating and/or to make it provide an improved barrier between the metal substrate and materials, for example water, with which it may come in contact and which are likely to be corrosive or to lift the paint from the surface. The reaction by which this fixing or immobilisation is accomplished may involve neutralization, double decomposition, esterification, resinification or organic complex formation. Generally two or more of these aspects may be present in each case.

Materials which may be used as the insolubilising ingredients of the insolubilising solution include salts of volatile acids, both organic and inorganic, preferably of metals having a valence of at least 2, although in

- some instances salts of the alkali metals may be used, particularly where they are in complex salts which also contain metals having a valence of at least two. Specific salts which may be used include nitrates, carbonates, halides, and acetates. Examples of suitable metal cations in these salts are iron, both ferric and ferrous, zinc and chromium. Additionally, amines may also be used such as the fatty acid aliphatic amines and diamines wherein the fatty acids are derived predominantly from tallow or coconut oil, tertiary alkyl amines, hexamethylenediamine, monoethanolamine, and amides, such as those derived from the condensation of unsaturated fatty acids such as dilinoleic acid with aliphatic amines such as ethylene diamine. Oxides and hydroxides, preferably of metals having a valence of at least two may also be used. Typical of these materials are the zinc oxides, zinc hydroxides, iron hydroxides, both ferric and ferrous, chromium hydroxides, and silicon dioxide, preferably as colloidal silica. Additionally, metallic salt-oxide complexes may also be used such as pigments like zinc yellow, and zinc tetroxy chromate. Other materials which may be used include various organic resins or polymeric materials such as melamine acrylic resins, urea-formaldehyde and amine resins, urea-aldehyde resins, epoxys such as those prepared by the reaction of epichlorohydrin and bisphenol, polyvinylacetals, such as polyvinylbutyral, and dimethylhydantoin-formaldehyde resin. Preferably, these latter two materials, i.e., the metal salt oxide complexes or pigments and the resin materials, are used together rather than separately, and desirably in a weight ratio of resin to pigment greater than 1.5:1. Various organic reductants may also be used such as dimethylolurea, hexamethylolmelamine hydroquinone, pyrocatechol, pyrogallol, p-methylamino-phenyl sulphate, and N-p-hydroxyphenylglycine.
- Trivalent chromium compounds such as chromium nitrate, chromium acetate, chromium carbonate, and chromium phosphate and organic complexes of trivalent chromium, such as methacrylate chromic chloride can also be used. Additionally, ammoniated oxides and ammoniated hydroxides of metals having a valence of at least two, for example, zinc, iron, both ferric and ferrous, and chromium, may also be used, either as such or in combination with colloidal silica. In many instances, with these materials, it is preferred also to include colloidal silica with the ammoniated oxide or hydroxide.
- Various combinations of resins, such as polyvinyl butyral and a pigment, such as zinc tetroxy chromate have given excellent results. Dimethylhydantoin-formaldehyde resin with zinc yellow has also given good results. Typical concentrations of insolubilising ingredients, or mixture or ingredients, are from 0.1 to 6% by weight of the solution applied, with concentrations of from 0.3 to 1% preferred. Typical of the amount of insolubilising ingredient which may be deposited may be from 1 to 100 mg/sq. foot, while amounts of from 15 to 500 mg/sq. foot are preferred.
- The insolubilising solution may be applied onto an unheated surface, for example a surface having a room temperature of, for example, from 65 to 75°F. Preferably however the surface onto which the composition is applied is preheated to a temperature of at least 175°F, preferably from 200 to 600°F although in general it is preferred that the upper limit on the temperature range should be below 350°F. The application may be effected by any convenient method, for example by roller coating, by immersing, by flooding or by spraying. However, the spraying technique described above and which which results in there being substantially no run-off is the preferred method of application. Provided that the conditions of application are appropriate the insolubilising ingredients bring about insolubilisation of the unreacted ingredients of the coating very quickly, the insolubilisation generally being effected substantially simultaneously with the application of the solution.
- It is well known that it is desirable to stabilise conversion coatings by treating them with a chromium-containing compound. This treatment, in conventional processes, generally takes the form of a chromate rinse. The stabilisation is carried out to improve the properties of the conversion coating. It is desirable to improve the properties of the conversion coatings formed in the process of the invention similarly, treating them with trivalent or hexavalent chromium as a stabiliser. The stabilising treatment may be effected by including a suitable chromium compound in the insolubilising solution or it may be effected by treating the coated surface with a chromium-containing stabilising solution subsequent to the insolubilisation of the coating. Examples of stabilising solutions which may be applied subsequently to the insolubilisation are acidic aqueous solutions or suspensions of chromates and dichromates of metals having a valency of at least two. Examples of such materials are zinc chromate and dichromate, aluminium chromate and dichromate, calcium chromate and dichromate, iron, both ferric and ferrous, chromate and dichromate, cobalt chromate and dichromate, and nickel chromate and dichromate. Additionally, in many instances, aqueous solutions of chromic acid ( $\text{CrO}_3$ ) may also be used. The chromic acid may be used as such, or if desired it may be combined with other materials, such as aluminum oxide, colloidal silica, water glass, solution of zinc oxide and ammonium hydroxide, or solutions of

zinc oxide and ammonium hydroxide containing silica. These latter mixtures, of chromic acid combined with other materials, are examples of solutions which act both as insolubilising and as stabilising solutions. When solutions such as these are used it is generally only necessary to carry out a two stage process, although even if a chromium containing insolubilising solution is used it is sometimes desirable still to subject the surface to a stabilising treatment. Examples of other solutions which may be used to effect both insolubilisation and stabilisation of the conversion coating are solutions of resin compositions such as dimethyl hydantoin-formaldehyde resins containing pigment materials such as the zinc yellows and zinc tetroxy chromate, zinc bichromate with colloidal silica, and ferric hydroxide and colloidal silica compositions containing chromic acid.

In some instances trivalent chromium may be used as the stabilising material, examples of suitable trivalent materials being chromium salts such as chromium acetate, chromium phosphate, chromium nitrate, and chromium carbonate. Additionally, organic complexes of trivalent chromium, such as methacrylate chromium chloride may also be used. Generally such trivalent chromium materials are used in the insolubilising composition, so that the application of a separate stabilizing composition may not be essential. However, in some instances, particularly when the conversion coating solution was based on phosphoric acid and auxiliary acid, a subsequent chromate rinse may be very desirable. When a chromate stabilising composition is applied as a separate step the concentration of chromate, calculated as  $\text{CrO}_3$ , is typically from 0.01 to 2% by weight, while amounts of from 0.1 to 1% are preferred. The preferred weight of coating obtained by the stabilising treatment may typically be between 0.1 and 20 mg/sq. ft. while weights of from 1 to 8 mg/sq. ft. are preferred. When the chromium stabilising compound is included in the insolubilising solution it is preferred that it is included in such amounts as to yield the same coating weights of chromate. The application of a chromium stabilising solution may be effected in any convenient manner, for example by immersion or by roller application, although spraying methods are preferred. The application can be effected on unheated surfaces, for example surfaces having room temperatures of for example, 65 to 75°F., although preferably the surfaces are preheated to temperatures above 200°F, maximum temperatures of up to 400°F, or more preferably up to 350°F, being permissible. It is particularly preferred to carry out the application by the spraying process described in detail above with a surface temperature of above 200°F.

The process of the invention is most conveniently carried out by passing the articles to be coated continuously through a series of spray zones in which the articles are subjected to either two or three different spray treatments, depending on whether or not the chromium stabiliser is included in the insolubilising solution. The articles being treated may, for example, be galvanised surfaces produced immediately previously by a hot dip process and may be in the form of sheet or coil. Typical of the speed of travel of the metal articles which may be used are speeds of 10 to about 500 feet per minute.

The process of the invention has many advantages. It is a high speed process and it can be carried out so that there is no need to subject the conversion coating to a rinse. The process can be carried out so that all the reacting solutions being used are used up at once with the result that there is no recycling of them. As a result the control of the process is very simple, there being no necessity to continuously analyse the solutions being used. The corrosion and paint adhesion properties of the coatings produced by the invention are good and the coatings prevent white corrosion on storage of hot-dip galvanised articles. The corrosion and paint adhesion properties of the coatings do, however, vary to a certain extent from one process to another and from one metal article to another. A further advantage of the invention is that it is possible to subject galvanised articles having the coatings to a subsequent temper roller without any undue loss of quality of the coatings produced. The coatings produced by the invention prevent staining of zinc surfaces during storage.

To exemplify the invention conversion coatings were formed by the process of the invention on galvanised surfaces produced by a high speed continuous hot dip process and the coated surfaces were painted with an alkyd-melamine baking enamel paint and then subjected to corrosion and paint adhesion tests. In each process galvanised surfaces were cleaned with solvent and then heated to a temperature of from 275 to 325°F, generally about 300°F and coatings were then formed by the process of the invention using the spray technique described in detail above. The conversion coating solutions generally contained about 1% phosphate, measured as  $\text{PO}_4$ , and were applied to yield a conversion coating weight of from 40 to 50 mg/foot. The insolubilising solution generally had a concentration of 0.4 percent and was applied at a coating rate of 15 to 35 milligrams per square foot while the stabilizing composition generally had a  $\text{CrO}_3$  content of 0.2 percent and was applied to yield a chromate coating weight of about 3 milligrams per square foot.

- One test carried out was the salt spray test ASTM B117—61 with painted panels scribed as given in ASTM test D—165461. This uses a 5 percent sodium chloride fog. The ratings given depend on the creepage from the scratch, given in 1/16 of an inch. Ratings given as spot (S) indicate no creepage except in a small area. In the humidity test, panels were exposed in a walk-in room at 100 percent relative humidity at 100°F, for the designated period of time. The blistering was rated according to ASTM designation D714—56 and is reported as follows. D—dense; MD medium dense; M—medium; FM—few medium; F—few; and VF—very few. In both the salt spray and humidity tests, unless otherwise indicated, the exposure time was 504 hours. In the physical test, adhesion is determined by knife blade and the results are reported on the scale of 0 to 10, where 10 is excellent, 8 is good, 6 is fair, 4 is poor, 2 is very poor, 0 is complete loss of adhesion. In the forming test, painted panels were subjected to a severe deformation producing parallel short radius right angle bends and paired three dimensional short radius shoulders in one operation. Failures or degrees thereof are shown by percentage peeling of the paint. The results are shown in the Table below. For comparative purposes similar processes and tests were carried out in which an insolubilising coating step was omitted. These examples are also included in the Table and are numbered with an X.
- 5
- 10
- 15
- 20
- 25
- 30
- 35

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
1 X	Zn and Ferrous phosphate solution, content 0.1% Zn, 0.15% Fe, 1% PO <sub>4</sub> and 0.05% HNO <sub>3</sub>	—	0.2% aqueous solution of CrO <sub>3</sub>	1-3	—	6-5	—
2	Same as 1	Solution of 0.4% ZnO in an 18:82 dilution of conc. NH <sub>4</sub> OH in water also containing 0.2% CrO <sub>3</sub> and 0.3% colloidal SiO <sub>2</sub>	—	0-1	—	9	—
3	Same as 1	ZnCr <sub>2</sub> O <sub>7</sub> (aqueous solution containing 0.2% CrO <sub>3</sub> )	—	1-4	F	7-6	35
4	Same as 1	Same as 3 plus 0.3% colloidal SiO <sub>2</sub>	—	0-1	F	10	23
5 X	Same as 1 but with 0.25% HNO <sub>3</sub>	—	0.2% aqueous solution of CrO <sub>3</sub>	1-5	M	6-4	65
6	Same as 5	1.5% aqueous solution of dimethylhydantoin form- aldehyde resin	0.2% aqueous solution of CrO <sub>3</sub>	0-3	F	10	2.5
7	Zn phosphate solution as disclosed in United States Patent No. 2,835,617	0.8% aqueous solution of melamine-formaldehyde resin	0.2% aqueous solution of CrO <sub>3</sub>	—	—	10	0
8	Ferrous phosphate sol. containing 1% PO <sub>4</sub> and 0.25% NO <sub>3</sub> and 0.15% Fe	0.05% aqueous sol. of N-P-hydroxyphenyl glycine	0.2% aqueous solution of CrO <sub>3</sub>	—	—	8	10

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
9 X	Same as 8	—	Same as 8	—	—	6	50
10	Same as 5	Same as 2 but without $\text{SiO}_2$	—	0-1	—	10	2.5
11	Same as 5	High molecular weight amine sold under the Trade Mark Amberlite LA-1	0.2% aqueous solution of $\text{CrO}_3$	1-3	—	10	0
12 X	Same as 8	—	Same as 8	—	(336 hours) D M	9	55
13	Same as 8	0.2% aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Same as 11	—	—	10	23
14 X	Same as 5	—	Same as 5	—	—	6-5	20
15	Same as 5	0.3% aqueous dispersion of $\text{CrPO}_4$	Same as 5	—	—	10	10
16	Same as 5	0.3% aqueous dispersion of colloidal $\text{SiO}_2$	Same as 5	—	—	10	13

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
17	Same as 5	0.3% aqueous dispersion of $\text{Al}_2\text{O}_3$	Same as 5	—	—	10	5
18	Same as 5	Same as 2 without $\text{CrO}_3$ and $\text{SiO}_2$	Same as 5	0—1	F	9—7	38
19	Same as 5	Same as 2 without $\text{SiO}_2$	—	0—1	F	10—8	28
20	Same as 5	Same as 2 without $\text{CrO}_3$	Same as 5	0—1 <sup>s</sup>	VF	10	25
21	Same as 5	Same as 2	—	0—1 <sup>s</sup>	FM	10	10
22	Same as 5	—	Same as 5	1—2	MD (336 hours)	7—4	—
23	Same as 5	0.4% aqueous suspension of $\text{ZnO}$	Same as 5	0—2	FM	10	13
24	Same as 5	0.8% aqueous suspension of $\text{ZnCO}_3$	Same as 5	0—1	VF	10	28



Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
In the following examples 25 to 28, a post-forming vinyl paint was substituted for the alkyd-melamine baking enamel prior to running the comparative tests.							
25	Same as 5	0.4% aqueous suspension of $\text{Fe}(\text{OH})_3$	Same as 5	—	—	10	0
26	Same as 5	Same as 28 plus 0.3% colloidal $\text{SiO}_2$	Same as 5	—	—	10	25
27	Same as 5	Same as 29 plus 0.2% $\text{CrO}_3$	—	—	—	10	0
28	Same as 5	—	Same as 5	—	—	7	0
29	Same as 5	—	Same as 5	1-2	(396 hours) MD	7-4	—
30	Same as 5	0.2% aqueous dispersion of $\text{Ba}(\text{OH})_2$	Same as 5	(336 hours) 0-3	MD	10	—
31 X	Same as 5	—	0.2% $\text{CrO}_3$	—	—	8	35
32	Same as 5	Aqueous solution of 0.2% $\text{CrO}_3$ and 0.3% colloidal $\text{SiO}_2$	—	—	—	10	15
33	Same as 5	Same as 35 except 0.3% $\text{SiO}_2$ present as a potassium silicate	—	—	—	10	2.5

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
34	Same as 5	Aqueous solution of 0.05% pyrocatechol and 0.3% colloidal $\text{SiO}_2$	0.2% $\text{CrO}_3$	—	—	9—5	7.5
35	Same as 5	Aqueous solution of 0.05% ethylene glycol and 0.3% colloidal $\text{SiO}_2$	0.2% $\text{CrO}_3$	—	—	10	5
36	Same as 8	Aqueous dispersion containing 0.5% polyvinyl butyral and 0.5% zinc tetroxy chromate	—	—	F	10	0
37	Same as 8	Same as 39 except with copolymer of butadiene and styrene	—	—	MD	10—9	2—5
38	Same as 8	Same as 39 except with copolymer of styrene and polyvinyl pyrrolidone	—	—	FM	10	0
39	Same as 8	Aqueous dispersion of 0.5% dimethylol urea and 0.2% of $\text{CrO}_3$ as $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$	—	0—1	F	8	5
40	Same as 8	Aqueous dispersion of 0.5% melamine-formaldehyde resin and 0.5% of zinc yellow ( $\text{KO}_2 \cdot 4\text{Zn} \cdot 0.4 \text{CrO}_3 \cdot 3\text{H}_2\text{O}$ )	—	0—1	VF	10	2.5
41 X	Same as 8	—	0.2% $\text{CrO}_3$	1—2	F	5	85

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
42	Same as 8	Aqueous dispersion of 1.5% dimethylhydantoin-formaldehyde resin and 0.5% zinc yellow	—	—	—	9	—
43 X	Zn—Ni solution containing 1.0% PO <sub>4</sub> , 0.5% NO <sub>3</sub> and 0.45% total Zn and Ni	—	Aqueous solution of 0.2% CrO <sub>3</sub>	(168 hours) 1—2	(48 hours) D	7	35
44	Same as 43	Same as 2 without CrO <sub>3</sub>	Same as 43	0—2 <sup>s</sup>	VF	10	5
45 X	Zn—Fe solution containing 1.0% PO <sub>4</sub> , 0.25% NO <sub>3</sub> and 0.1—0.3% Zn and Fe	—	Same as 43	1—1	FM	9	2.5
46	Same as 45	Same as 44	Same as 43	0—1 <sup>s</sup>	VF	10	0
47 X	Same as 45 except Ca substituted for Fe	—	Same as 43	1—3	(48 hours) D	9	15
48	Same as 47	Same as 44	Same as 43	0—3 <sup>s</sup>	F	10	10
49 X	Same as 45 except Mn substituted for Zn and Fe	—	Same as 43	1—2	FM	8	10
50	Same as 49	Same as 44	Same as 43	0—1 <sup>s</sup>	F	10	15
51 X	Same as 49 except Ni substituted for Mn	—	Same as 43	(168 hours) 1—3	(48 hours) D	8	7.5

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
52	Same as 51	Same as 44	Same as 43	10	(336 hours) M	10	2.5
53 X	Same as 49 except Ca substituted for Mn	—	Same as 49	2—3	(48 hours) D	9	43
54	Same as 53	Same as 44	Same as 53	0—2 <sup>s</sup>	FM	10	45
55	Same as 5	Same as 44	Same as 6	0—3 <sup>s</sup>	VF	9.5	2.5
56	Same as 5 except glycolic acid instead of HNO <sub>3</sub>	Same as 44	Same as 6	0—1 <sup>s</sup>	VF	10	30
57	Same as 5 except acrylic acid instead of HNO <sub>3</sub>	Same as 44	Same as 6	0—1 <sup>s</sup>	VF	9	45
58	Same as 5 except adipic acid instead of HNO <sub>3</sub>	Same as 44	Same as 6	0—3 <sup>s</sup>	VF	10	40
59	Same as 5 except hydroxy-methyl phosphonic acid instead of HNO <sub>3</sub>	Same as 44	Same as 6	0—1 <sup>s</sup>	VF	9—10	40
60	1.0% hydroxymethyl phosphonic acid containing 0.14% Fe	Same as 55	Same as 6	—	—	9—10	—

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
61 X	Aqueous solution of 1% $H_3PO_4$ and 0.05% $HNO_3$	—	Aqueous solution of 0.2% $CrO_3$	(48 hrs.) 1—3	(48 hrs.) MD	7	45
62	Same as 61	18:82 dilution of concentrated $NH_4OH$ in $H_2O$ and containing 0.4% $ZnO$	Same as 61	0—1	M	10—9	40
63 X	Same as 61 but with 0.25% $HNO_3$	—	Same as 61	0—1 5 S	(48 hrs.) D	2	85
64	Same as 63	0.4% suspension of $CrPO_4$	Same as 61	0—1	F	10	64
65	Same as 63	Aqueous dispersion containing 0.8% polyvinyl butyral and 0.5% zinc yellow	—	0—1 4 S	VF	7	75
66	Same as 63	Same as 62 plus 0.3% $SiO$ and 0.2% $CrO_3$	—	0—1 S	(48 hrs.) D	9	75
67	Same as 63	Aqueous dispersion of 1.5% dimethyl hydantoin formaldehyde resin and 0.5% zinc yellow	—	1—3	(48 hrs.) D	8	78

Example	Conversion Coating Solution	Insolubilising Solution	Stabilising Coating Solution	Salt Spray	Humidity	Knife Adhesion	Forming (% Peel)
68	Same as 61	Same as 62 plus 0.3% SiO <sub>2</sub>	Same as 61	0-1 S	FM	4	98
69 X	Same as 61	—	Same as 61	(168 hrs.) 1-2 5 S	D	6	25
70	Same as 61	Aqueous dispersion of 3.0% dimethyl hydantoin formaldehyde resin	Same as 61	1-2	D	9	5
71 X	Same as 61	—	Same as 61	(48 Hrs.) 1-2 3 S	(168 Hrs.) D	5	53
72	Same as 61	Same as 62 plus 0.2% CrO <sub>3</sub>	—	0-3 S	FM	8	55
73 X	Same as 61	—	Same as 61	0-2 4 S	(24 Hrs.)	5	75
74	Same as 61	Aqueous dispersion of 0.3% SiO <sub>2</sub> and 0.2% CrO <sub>3</sub>	—	(168 Hrs.) 0-3 4 S	MD	7	63
75	Same as 61	Same as 62	Aqueous dispersion of 0.3% SiO and 0.2% CrO <sub>3</sub>	1-2 3 S	(48 Hrs.) D	9	2.5
76	Same as 61	Same as 62	Same as 75 with sodium silicate substituted for SiO <sub>2</sub>	0-3 4 S	(48 hrs.)	9	50
77	Same as 61	Same as 68 with sodium silicate substituted for SiO <sub>2</sub>	Same as 61	0-1	(24 hrs.) D	8	20

## EXAMPLE 78

The procedures of Examples 36, 37 and 38 were repeated with the exception that the coating compositions were applied to panels of cold rolled steel, rather than zinc panels. Additionally, in the case of Example 36, the quantities of the components of the immobilizing coating composition were quadrupled and in the case of Examples 37 and 38, the amounts of these components were doubled. In each instance, the knife adhesion and forming test results were 10 and 0, respectively.

## EXAMPLE 79

A series of runs was made wherein the conversion coating was an aqueous solution containing from 0.1 to 0.5 percent acetic acid and oxalic acid in the amounts of 0.1, 0.2, 0.5, and 1 percent. In the four runs made, the temperatures of the galvanised panels onto which the coating was misted were 200°F, 250°F, 300°F, and 375°F. In each instance, the application of the conversion coating material was followed by a mist-on application of a 0.2 percent aqueous solution of CrO<sub>3</sub>. The typical results obtained on testing the painted panels showed from 0 to 3 creepage after 504 hours in the salt spray, blister failure only after 504 hours in the humidity test and fair to good knife adhesion and forming tests.

## EXAMPLE 80

The procedure of Example 79 was repeated with the exception that the conversion coating composition was a ferric oxalate solution containing 0.5 percent iron which was applied to panels which were at a temperature of 375°F. The test results on the painted panels showed good humidity and physical test ratings.

## EXAMPLE 81

Galvanised panels were preheated to provide surfaces at 300°F. The ferrous phosphate conversion coating solution of Example 5 was then misted onto these surfaces in a series of runs designed to obtain a wide range of coating weights on the surface. In the first series of runs, the number of passes of the spray gun over the surface was varied from 1 to 4 and the coating weights obtained varied in the amount of PO<sub>4</sub> from 29 to 86 milligrams per square foot. In the next series of runs, the times for each pass over the panels were varied from 1—6 seconds and coating weight variations, in terms of

PO<sub>4</sub> content were obtained within the range of about 14 to about 83 milligrams per square foot. In the third series, the PO<sub>4</sub> concentration of the ferrous phosphate solution was varied within the range of about 0.5 to about 5 percent and there were obtained coating weights within the range of about 20 to about 250 milligrams PO<sub>4</sub> per square foot. Thereafter, in each instance, an aqueous CrO<sub>3</sub> solution was misted onto the panels to provide a coating containing 3 milligrams per square foot of CrO<sub>3</sub>. The paint bonding performances of the surfaces produced were then evaluated and in all instances, these were acceptable although better paint bonding was obtained when the PO<sub>4</sub> coating weight was within the range of about 20 to about 100 milligrams per square foot.

## EXAMPLE 82

The procedure of the preceding Example was repeated several times using the following temperatures of the zinc metal surface being coated: 175°, 200°, 225°, 275°, 300°, 325°, 375°, 400°, 425° and 500°F. In each instance, an excellent coating was obtained, although at the lowest temperatures of 175°F, the coating was somewhat spotted.

## EXAMPLE 83

The procedure of Example 20 was repeated using the same conversion coating composition followed by the immobilizing composition of Example 20 and the stabilizing composition of Example 6. In this example, however, these coatings were applied to panels of cold rolled steel and aluminium, rather than zinc. In each instance, the coating obtained gave very good results in the salt spray and humidity test and a 10 rating in the knife adhesion and no peeling in forming tests were obtained, respectively.

## EXAMPLE 84

A phosphate composition which was .01 molar Zn, .01 molar Ni, 0.1 molar PO<sub>4</sub>, 0.04 molar NO<sub>3</sub> was misted onto commercial galvanised panels to provide 40—50 milligrams PO<sub>4</sub> per square foot, after which a fixer solution containing 1.5 percent dimethylhydantoin-formaldehyde resin and sufficient zinc dichromate to give 0.2 percent CrO<sub>3</sub> was misted on, at a rate to provide 3 milligrams CrO<sub>3</sub> per square foot. The panels were then painted with a vinyl baking paint and excellent salt spray, humidity and physical tests were obtained as shown below:

	Salt Spray	Humidity	Adhesion	Forming
Zincdichromate control	N,*	VF, F	3	80% peel
DMHF Zinc dichromate	N,N	VF, F	10	0

N = zero creepage

\* failed in 48 hrs. (major peeling)

#### EXAMPLE 85

5 A ferrous phosphate solution containing 1.8%  $\text{PO}_4$ , 0.25%  $\text{NO}_3$ , 0.15% Fe was misted on 300°F galvanised panels to give 40—50 milligrams  $\text{PO}_4$  per square foot and was followed by an aqueous resin soluble chromate composition, misted on to provide 3 milligrams  $\text{CrO}_3$  per square foot. This 10 latter composition contained 1.5 percent dimethylhydantoin-formaldehyde resin and sufficient zinc dichromate solution to give 0.2 percent  $\text{CrO}_3$ . On panels painted with a high temperature baking vinyl, this treat- 15 ment improved the knife adhesion from 7 to 10, when compared to the use of zinc dichromate without the resin present.

#### EXAMPLE 86

20 A series of zinc and nickel phosphate solutions were misted onto commercial galvanised panels at 300°F in an amount to obtain a coating weight of 40—50 milligrams  $\text{PO}_4$  per square foot.

25 The metal content of the phosphate solutions was .02 molar with approximately 0.1 molar  $\text{PO}_4$  and 0.04 molar  $\text{NO}_3$ . The Zn/Ni ratio was varied as follows: 1:0, 2:1, 1:1, 1:2, and 0:1. A further variant was introduced by adding  $\text{H}_2\text{SiF}_6$  at 0.0 to 0.2 percent. 30

The phosphate coating was followed quickly with a fixer prepared from: zinc yellow pigment 0.5%;  $\text{SiO}_2$  0.05% dimethylhydantoin-formaldehyde resin 1.5%. 35

This composition was misted to provide approximately 3 milligrams  $\text{CrO}_3$  per square foot.

40 These coatings were painted with a high temperature vinyl composition. All variants showed excellent performance in accelerated and physical tests.

A similar series was made with the metal level raised to 0.05 molar also with excellent results. 45

50 The process of Examples 61 to 77 have been repeated using other auxiliary acids including chromic acid, glycolic acid, acrylic acid, adipic acid, hydroxymethyl phosphonic acid and other insolubilising materials including tertiary alkyl amines, hexamethylene diamine, monoethanol amine, butanol, polypropylene glycol, resorcinol, dimethylol urea, hexamethylol melamine, hydroquinone, pyro-

gallol and ammoniated iron oxide and the like, applied both to metal heated before and after the application of the conversion coating, using roll-on and immersion techniques as well as spraying techniques, and comparable results were obtained. 55

#### WHAT WE CLAIM IS:—

60 1. A process for forming a protective coating on a metal surface which comprises preheating the metal and spraying onto it a conversion coating solution of which the principal coating-forming ingredient is a coating phosphate, a coating oxalate, a coating acetate or phosphoric acid with an auxiliary acid, the temperature of the metal and the quantity of the solution applied being such that there is substantially no run-off of solution and a dry conversion coating is formed part of which at least is soluble, and then, without any intermediate rinsing step, rendering the coating totally insoluble by applying to it an insolubilising solution which reacts with the soluble components of the conversion coating to form insoluble products. 65 70 75

2. A process according to claim 1 in which the insolubilising solution contains trivalent or hexavalent chromium. 80

3. A process according to claim 1 in which the protective coating formed is subsequently treated with a solution containing hexavalent chromium. 85

4. A process for forming a protective coating on a metal surface which comprises preheating the metal and spraying onto it a conversion coating solution of which the principal coating-forming ingredients is a coating phosphate or is phosphoric acid with an auxiliary acid, the temperature of the metal and the quantity of the solution applied being such that there is substantially no run-off of solution and a dry phosphate conversion coating is formed in which there remains unreacted, soluble coating-forming ingredient, and then, without any intermediate rinsing step, rendering the coating totally insoluble by applying to it an insolubilising solution which reacts with the unreacted coating-forming ingredient by double decomposition, neutralisation, esterification, resinification or organic complex formation to form insoluble products, the protective coating being stabilised 90 95 100 105



by including trivalent or hexavalent chromium in the insolubilising solution or by subsequently treating it with a solution containing hexavalent chromium.

5 5. A process according to any one of the preceding claims in which the metal surface is a zinc surface.

10 6. A process according to claim 5 in which the zinc surface is formed by hot galvanising a ferrous surface and the conversion coating solution is applied to the galvanised surface while this is still hot from the galvanising.

15 7. A process according to claim 6 in which the protective coating is subsequently stabilised by spraying it with a solution containing hexavalent chromium while the surface is still hot.

20 8. A process according to any one of the preceding claims in which the conversion coating solution contains from 0.3 to 6.0% by weight of coating phosphate, (measured as  $\text{PO}_4$ ).

25 9. A process according to any one of claims 1 to 7 in which the conversion coating solution contains from 0.3 to 6.0% by weight of phosphoric acid (measured as  $\text{PO}_4$ ) and contains also an auxiliary acid in a proportion of phosphoric acid to auxiliary acid of from 100:1 to 2:1.

30 10. A process according to claim 9 in which the proportion of phosphoric acid to auxiliary acid is from 10:1 to 4:1.

35 11. A process according to any one of the preceding claims in which the auxiliary acid is nitric acid.

12. A process according to any one of the preceding claims in which the conversion coating solution additionally contains an accelerator.

13. A process according to any one of the preceding claims in which the insolubilising solution contains as insolubilising ingredient a salt of a metal having a valency of greater than 2 with a volatile acid, an ammoniated oxide or hydroxide of such a metal, a metal salt-oxide complex, an amine, an organic resin, a mono-, di-, or poly-hydroxy alcohol, an organic reductant, or an organic complex of trivalent chromium.

14. A process according to any one of claims 1 to 12 in which the insolubilising solution contains as insolubilising ingredient colloidal silica, alone or with other insolubilising ingredients.

15. A process according to claim 13 in which the insolubilising ingredient is zinc oxide or zinc hydroxide dissolved in ammonia.

16. A process according to claim 15 in which the solution additionally contain colloidal silica.

17. A process according to claim 13 in which the insolubilising coating solution is an aqueous solution of dimethyl hydantoin-formaldehyde resin.

18. A process according to claim 17 in which the aqueous solution additionally contains zinc yellow pigment.

19. A process according to claim 1 substantially as herein described with reference to any one of the Examples.

20. Articles coated with a protective coating by a process according to any preceding claim.

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